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Application of Markov Chain Calculations to the Study of Penultimate-Unit Effects in Terpolymerization

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SUMMARY

Equations are derived for assessing the effects due to penultimate units in terpolymerization on composition equations. Equations of varying scope are offered for the penultimate-unit effects indicated. In all the examples treated, one monomer is assumed to be incapable of self-propagation.

Although penultimate-unit effects in binary copolymerization have been well described and appropriately treated mathematically by the use of Markoffian techniques [1, 2], such effects in terpolymerization have received relatively little attention [3]. It is the purpose of this paper to treat special cases of either demonstrated or suspected importance experimentally, rather than to attempt an exhaustive inspection of all possible variations. Nevertheless, for descriptive purposes for the hypothetical case where all terpolymer states are possible and all nine penultimate combinations influence addition, the transition matrix shown on page 878 may be set up.

It is probably pointless to derive composition equations for this general case because of their exceeding complexity and lack of probable application.

One of the most fruitful areas in which to seek penultimate-unit effects is in monomer combinations containing one or more monomers incapable of self-propagation. The most frequently encountered source of penultimate-unit effects is repulsion of adding monomer by penultimate monomer units. Obviously monomers failing in

$$
\begin{array}{ll}
 & \text{Initial} \\
\text{Final} &
\begin{array}{c}
 \\ M_1M_1 \\ M_1M_2 \\ M_1M_3 \\ M_2M_1 \\ M_2M_2 \\ M_2M_3 \\ M_3M_1 \\ M_3M_2 \\ M_3M_3
\end{array}
\left[\begin{array}{ccccccccc}
M_1M_1 & M_1M_2 & M_1M_3 & M_2M_1 & M_2M_2 & M_2M_3 & M_3M_1 & M_3M_2 & M_3M_3 \\
P_{11} & 0 & 0 & P_{41} & 0 & 0 & P_{71} & 0 & 0 \\
P_{12} & 0 & 0 & P_{42} & 0 & 0 & P_{72} & 0 & 0 \\
1-P_{11}-P_{12} & 0 & 0 & 1-P_{41}-P_{42} & 0 & 0 & 1-P_{71}-P_{72} & 0 & 0 \\
0 & P_{21} & 0 & 0 & P_{51} & 0 & 0 & P_{81} & 0 \\
0 & P_{22} & 0 & 0 & P_{52} & 0 & 0 & P_{82} & 0 \\
0 & 1-P_{21}-P_{22} & 0 & 0 & 1-P_{51}-P_{52} & 0 & 0 & 1-P_{81}-P_{82} & 0 \\
0 & 0 & P_{31} & 0 & 0 & P_{61} & 0 & 0 & P_{91} \\
0 & 0 & P_{32} & 0 & 0 & P_{62} & 0 & 0 & P_{92} \\
0 & 0 & 1-P_{31}-P_{32} & 0 & 0 & 1-P_{61}-P_{62} & 0 & 0 & 1-P_{91}-P_{92}
\end{array}\right]
\end{array}
\qquad [A]
$$

Initial

Final	M_1M_1	M_1M_2	M_1M_3	M_2M_1	M_2M_2	M_2M_3	M_3M_1	M_3M_2
M_1M_1	P_{11}	0	0	P_{41}	0	0	P_{71}	0
M_1M_2	P_{12}	0	0	P_{42}	0	0	P_{72}	0
M_1M_3	$1 - P_{11} - P_{12}$	0	0	$1 - P_{41} - P_{42}$	0	0	$1 - P_{71} - P_{72}$	0
M_2M_1	0	P_{21}	0	0	P_{51}	0	0	P_{81}
M_2M_2	0	P_{22}	0	0	P_{52}	0	0	P_{82}
M_2M_3	0	$1 - P_{21} - PP_{22}$	0	0	$1 - P_{51} - P_{52}$	0	0	$1 - P_{81} - P_{82}$
M_3M_1	0	0	P_{31}	0	0	P_{61}	0	0
M_3M_2	0	0	$1 - P_{31}$	0	0	$1 - P_{61}$	0	0

[B]

self-propagation due to repulsion of like units might be expected to exhibit residual effects at the penultimate position.

It is important to point out that in the case of self-propagating monomers exhibiting penultimate-unit effects (such as acrylonitrile) the equations to be derived will hold essentially in those regions where self-propagation is negligible.

TERPOLYMERIZATIONS WHERE ALL POSSIBLE PENULTIMATE UNIT EFFECTS OCCUR BUT M_3 DOES NOT ADD TO $M_3\cdot$

A regular transition matrix is set up (page 879). In this case, the imposed restriction of M_3 not adding to $M_3\cdot$ limits the number of possible states to eight.

Of course, it follows that the states M_1M_3 and M_2M_3 can only move individually to two states. For convenience the states indicated above are expressed as 0, M_1M_1; 1, M_1M_2; 2, M_1M_3; 3, M_2M_1; 4, M_2M_2; 5, M_2M_3; 6, M_3M_1; 7, M_3M_2.

To determine the limiting vector $\boldsymbol{\alpha}$ $(a_0, a_1, a_2, a_3, a_4, a_5, a_6, a_7)$ we must find a probability vector such that $\boldsymbol{\alpha}P = \boldsymbol{\alpha}$. In other words, Eqs. (1)-(9) must be satisfied for our matrix system.

$$1 = a_0 + a_1 + a_2 + a_3 + a_4 + a_5 + a_6 + a_7 \tag{1}$$

$$a_0 = P_{11}a_0 + P_{41}a_3 + P_{71}a_6 \tag{2}$$

$$a_1 = P_{12}a_0 + P_{42}a_3 + P_{72}a_6 \tag{3}$$

$$a_2 = (1 - P_{11} - P_{12})a_0 + (1 - P_{41} - P_{42})a_3 + (1 - P_{71} - P_{72})a_6 \tag{4}$$

$$a_3 = P_{21}a_1 + P_{51}a_4 + P_{81}a_7 \tag{5}$$

$$a_4 = P_{22}a_1 + P_{52}a_4 + P_{82}a_7 \tag{6}$$

$$a_5 = (1 - P_{21} - P_{22})a_1 + (1 - P_{51} - P_{52})a_4 + (1 - P_{81} - P_{82})a_7 \tag{7}$$

$$a_6 = P_{31}a_2 + P_{61}a_5 \tag{8}$$

$$a_7 = (1 - P_{31})a_2 + (1 - P_{61})a_5 \tag{9}$$

At this point it is desirable to invoke the assumption of statistical stationarity [4] or equivalence of reversed sequences [5]. Whether this assumption is valid in terpolymerization has been the subject of much debate. In the long run, the issue will stand or fall on the basis of whether results generated through the use of the concept are consistent with reality. On this tentative basis we employ the concept.

Thus we may set

$$a_1 = a_3 \tag{10}$$

$$a_2 = a_6 \tag{11}$$

$$a_5 = a_7 \tag{12}$$

Solved in terms of a_2, these results follow:

$$a_0 = -\frac{P_{41}a_2[P_{12}P_{71} + P_{72}(1 - P_{11})]}{[P_{12}P_{41} - (1 - P_{11})(1 - P_{42})][1 - P_{11}]} + \frac{P_{71}a_2}{1 - P_{11}} \tag{13}$$

$$a_1 = -\frac{a_2[P_{12}P_{71} + P_{72}(1 - P_{11})]}{P_{12}P_{41} - (1 - P_{11})(1 - P_{42})} \tag{14}$$

$$a_4 = -\frac{P_{22}a_2[P_{12}P_{71} + P_{72}(1 - P_{11})]}{[P_{12}P_{41} - (1 - P_{11})(1 - P_{42})(1 - P_{52})]} + \frac{P_{82}a_2(1 - P_{31})}{P_{61}(1 - P_{52})} \tag{15}$$

$$a_5 = \frac{a_2(1 - P_{31})}{P_{61}} \tag{16}$$

The differential terpolymer composition equation for these stated circumstances follows:

$$\frac{dM_1}{dM_3} = \frac{m_1}{m_3} = \frac{a_0 + a_3 + a_6}{a_2 + a_5} \tag{17}$$

It is seen that the numerator contains states which "generate" M_1 units and the denominator, states which generate M_3's. Substitution leads to

$$\frac{dM_1}{dM_3} = \frac{m_1}{m_3} = \frac{[AP_{71} - B(1 + P_{41} - P_{11})/A(1 - P_{11})] + 1}{[(1 - P_{31})/P_{61}] + 1} \tag{18}$$

where

$$A = [P_{12}P_{41} - (P_{11} - 1)(P_{42} - 1)] \tag{19}$$

$$B = [P_{12}P_{71} - P_{72}(P_{11} - 1)] \tag{20}$$

Similarly, it can be shown that

$$\frac{dM_2}{dM_3} = \frac{m_2}{m_3} = \frac{A(1 - P_{31})(1 + P_{82} - P_{52}) - BP_{61}(1 + P_{22} - P_{52})}{A(1 - P_{52})(1 + P_{61} - P_{31})} \tag{21}$$

TERPOLYMERIZATIONS WHERE PENULTIMATE-UNIT EFFECTS ARE LIMITED TO M_3 BEFORE $M_1\cdot$ AND TO M_1 AND M_2 BEFORE $M_3\cdot$ (NO ADDITIONS OF M_3 TO $M_3\cdot$)

In this example (page 883), matrix [B] has been simplified by allowing

$$P_{11} = P_{41}$$

$$P_{12} = P_{42}$$

$$P_{21} = P_{51} = P_{81}$$

$$P_{22} = P_{52} = P_{82}$$

Equation (18) reduces to

$$\frac{m_1}{m_3} = \frac{[(1 - P_{73})/P_{13}] + 1}{[(1 - P_{31})/P_{61}] + 1} \tag{22}$$

and Eq. (21) to

$$\frac{m_2}{m_3} = \frac{P_{13}(1 - P_{31}) + BP_{61}}{P_{13}(1 - P_{22})(1 - P_{31} + P_{61})} \tag{23}$$

Now, if the assumption is made that the probabilities of going from state M_1M_3 to states M_3M_1 and M_3M_2 are the same as the probabilities of going from state M_2M_3 to states M_3M_1 and M_3M_2, that is, that no penultimate-unit effect exists for monomer units

$$
\begin{array}{c|cccccccc}
 & M_1M_1 & M_1M_2 & M_1M_3 & M_2M_1 & M_2M_2 & M_2M_3 & M_3M_1 & M_3M_2 \\
\hline
M_1M_1 & P_{11} & 0 & 0 & P_{11} & 0 & 0 & P_{71} & 0 \\
M_1M_2 & P_{12} & 0 & 0 & P_{12} & 0 & 0 & P_{72} & 0 \\
M_1M_3 & 1-P_{11}-P_{12} & 0 & 0 & 1-P_{11}-P_{12} & 0 & 0 & 1-P_{71}-P_{72} & 0 \\
M_2M_1 & 0 & P_{21} & 0 & 0 & P_{21} & 0 & 0 & P_{21} \\
M_2M_2 & 0 & P_{22} & 0 & 0 & P_{22} & 0 & 0 & P_{22} \\
M_2M_3 & 0 & 1-P_{21}-P_{22} & 0 & 0 & 1-P_{21}-P_{22} & 0 & 0 & 1-P_{21}-P_{22} \\
M_3M_1 & 0 & 0 & P_{31} & 0 & 0 & P_{61} & 0 & 0 \\
M_3M_2 & 0 & 0 & 1-P_{31} & 0 & 0 & 1-P_{61} & 0 & 0
\end{array}
\qquad [C]
$$

preceding M_3, an interesting simplification of the composition equation results. Note that "statistical stationarity" is not violated in the assumption that a penultimate-unit effect due to M_3 does not require a penultimate-unit effect preceding $M_3\cdot$ radical. We obtain

$$\frac{m_1}{m_3} = P_{31}\left\{\frac{(P_{71} + P_{72})}{P_{13}} + 1\right\} \tag{24}$$

$$\frac{m_2}{m_3} = \frac{P_{13}(1 - P_{31}) + BP_{31}}{P_{13}(1 - P_{22})} \tag{25}$$

If the appropriate penultimate units are shown as the first of three integers in subscripts we obtain

$$\frac{m_1}{m_3} = P_{31}\left\{\frac{1 - P_{313} + P_{113}}{P_{113}}\right\} \tag{26}$$

In the event that monomers 1 and 3 are equivalent at the penultimate position (that is, that there is no penultimate-unit effect), Eq. (24) reduces to

$$\frac{m_1}{m_3} = \frac{P_{31}}{P_{13}} \tag{27}$$

which is the simplified terpolymer equation [5].

Similarly, Eq. (25) reduces to

$$\frac{m_2}{m_3} = \frac{P_{13}(1 - P_{31}) + P_{12}P_{31}}{P_{13}(1 - P_{22})} \tag{28}$$

when monomers 1 and 3 are equivalent at the penultimate position.

Applying the relationship [5]

$$P_{12}P_{23}P_{31} = P_{13}P_{32}P_{21} \tag{29}$$

further simplification occurs to yield

$$\frac{m_2}{m_3} = \frac{P_{32}}{P_{23}} \tag{30}$$

which is another form of the simplified terpolymer equation.

FORMAL SIMPLIFICATIONS OF MATRIX [B] WHERE ALL PENULTIMATE EFFECTS ARE POSSIBLE EXCEPT WHERE M_1 AND M_2 PRECEDE $M_1\cdot$

Starting with Eqs. (18) and (21), P_{11} is set equal to P_{41} and P_{12} equal to P_{42}. One obtains

$$\frac{m_1}{m_3} = \frac{[(1 - P_{73})/P_{13}] + 1}{[(1 - P_{31})/P_{61}] + 1} \tag{22}$$

$$\frac{m_2}{m_3} = \frac{P_{13}(1 - P_{31})(1 + P_{82} - P_{52}) + BP_{61}(1 + P_{22} - P_{52})}{P_{13}(1 - P_{52})(1 + P_{61} - P_{31})} \tag{31}$$

Eliminating all penultimate-unit effects before $M_1\cdot$ one sets

$$P_{11} = P_{41} = P_{71}$$

$$P_{12} = P_{42} = P_{72}$$

and obtains

$$\frac{m_1}{m_3} = \frac{P_{61}}{P_{13}(1 - P_{31} + P_{61})} \tag{32}$$

$$\frac{m_2}{m_3} = \frac{P_{13}(1 - P_{31})(1 + P_{82} - P_{52}) + P_{12}P_{61}(1 - P_{52} + P_{22})}{P_{13}(1 - P_{52})(1 - P_{31} + P_{61})} \tag{33}$$

Setting

$$P_{11} = P_{41} = P_{71}$$

$$P_{12} = P_{42} = P_{72}$$

$$P_{51} = P_{81}$$

$$P_{52} = P_{82}$$

one obtains

$$\frac{m_1}{m_3} = \frac{P_{61}}{P_{13}(1 - P_{31} + P_{61})} \tag{32}$$

$$\frac{m_2}{m_3} = \frac{P_{13}(1 - P_{31}) + P_{12}P_{61}(1 - P_{52} + P_{22})}{P_{13}(1 - P_{52})(1 - P_{31} + P_{61})} \tag{34}$$

Elimination of all remaining penultimate effects except those preceding $M_3\cdot$ by setting

$$P_{21} = P_{51}$$

$$P_{22} = P_{52}$$

yields

$$\frac{m_1}{m_3} = \frac{P_{61}}{P_{13}(1 - P_{31} + P_{61})} \tag{32}$$

$$\frac{m_2}{m_3} = \frac{P_{13}(1 - P_{31}) + P_{12}P_{61}}{P_{13}(1 - P_{22})(1 - P_{31} + P_{61})} \tag{35}$$

Setting $P_{12}P_{23}P_{61} = P_{13}P_{32}P_{21}$, the condition of equivalence of reversed sequences,

$$\frac{m_2}{m_3} = \frac{P_{32}}{P_{23}(1 - P_{31} + P_{61})} \tag{36}$$

Of course, setting $P_{31} = P_{61}$ eliminates remaining penultimate effects:

$$\frac{m_1}{m_3} = \frac{P_{31}}{P_{13}} \tag{27}$$

$$\frac{m_2}{m_3} = \frac{P_{32}}{P_{23}} \tag{30}$$

It should be noted that Eq. (24) treats a single penultimate-unit effect in a terpolymerization where the monomer causing the effect does not homopropagate.

$$\frac{m_1}{m_3} = P_{31}\left(\frac{1 - P_{73}}{P_{13}} + 1\right) \tag{24}$$

If monomer 2 is allowed to disappear and the subscripts take on the significance earlier ascribed for penultimate effects where present,

$$\frac{m_1}{m_3} = \frac{P_{311} + P_{113}}{P_{113}} \tag{37}$$

which is a binary composition equation [6] equivalent to the Barb equation [7] for penultimate-unit effects where one monomer does not homopropagate.

REFERENCES

[1] F. P. Price, *J. Chem. Phys.*, **31** (1), 209 (1962).
[2] G. E. Ham, *J. Polymer Sci.*, **A2**, 3633 (1964).
[3] G. E. Ham, *J. Polymer Sci.*, **A2**, 4191 (1964).
[4] B. D. Coleman and T. G. Fox, *J. Polymer Sci.*, **A1**, 3183 (1963).
[5] G. E. Ham, *J. Polymer Sci.*, **A2**, 2735 (1964).
[6] G. E. Ham, *Copolymerization*, Wiley-Interscience, New York, 1964, p. 1.
[7] W. G. Barb, *J. Polymer Sci.*, **11**, 117 (1953).

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